



Short communication

Tris(pentafluorophenyl) borane-containing electrolytes for electrochemical reversibility of lithium peroxide-based electrodes in lithium–oxygen batteries

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H I G H L I G H T S

- ▶ TPFPB reduces the charge potential of Li_2O_2 -based electrode.
- ▶ TPFPB mitigates the formation of Li_2CO_3 by the electrochemical decomposition of EC and EMC.
- ▶ The electrochemical reversibility of Li_2O_2 -based electrode is improved in the presence of TPFPB.

A R T I C L E I N F O

Article history:

Received 16 July 2012

Received in revised form

27 September 2012

Accepted 12 October 2012

Available online 22 October 2012

Keywords:

Lithium–oxygen battery

Lithium peroxide

Electrolyte

Tris(pentafluorophenyl) borane

Solid electrolyte interphase

A B S T R A C T

Tris(pentafluorophenyl) borane (TPFPB) is evaluated as an additive for improving electrochemical performance of lithium peroxide (Li_2O_2)-based electrodes. It is found that TPFPB significantly reduced the charge potential of Li_2O_2 -based electrodes during the first charge process and improved reversible capacity during cycling without adding air (or O_2) to the cell. To confirm the effect of TPFPB on electrolyte decomposition, the surface chemistry of Li_2O_2 -based electrodes cycled in electrolytes with and without TPFPB was investigated.

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1. Introduction

Rechargeable Li–air batteries have attracted much attention as promising candidates for use in electric vehicles because such batteries can theoretically store 5–10 times more energy than current Li–ion batteries [1–3]. However, a significant technical challenge for the implementation of Li–air batteries is to ensure a reversible reaction [2,4]. Li–air batteries rely on the use of oxygen (or, ideally, ambient air) to form the solid products (Li_2O or Li_2O_2) during discharge and oxidation of lithium oxides to lithium and gaseous oxygen, which occurs upon subsequent charging. The insoluble solid reaction products in the organic electrolytes are accumulated within the pores of the air electrode and impede the rechargeability of Li–air batteries [2,3]. To avoid the precipitation of reaction products and the passivation of the electrode surface,

appropriate polar solvents are required to dissolve these solid products [5]. Organic carbonate-based electrolytes have been the most widely used electrolyte in Li– O_2 cells [1,2,6]. Such electrolytes, however, decompose in Li– O_2 cells on discharge, rather than forming Li_2O_2 , and in the process Li_2CO_3 and lithium-containing compounds are formed in the air electrode [7–9]. Recently, it was reported that organic carbonate-based electrolytes decompose at the cathode and that a mixture of lithium propyl dicarbonate, Li_2CO_3 , HCO_2Li , $\text{CH}_3\text{CO}_2\text{Li}$, CO_2 , and H_2O is formed on discharge [7]. In this regard, it was also reported that cyclic and linear carbonates, commonly used solvents in Li–ion batteries, are unstable in the presence of superoxide anion radical ($\text{O}_2^{\cdot-}$) [9]. The development of appropriate electrolytes is one prerequisite that is necessary to assure the long term stability of Li–air batteries.

Even though various cathode catalysts including carbon, metal oxides, and noble metals have been applied to enhance the sluggish kinetics of the oxygen reduction reaction and oxygen evolution reaction at the air electrode, Li– O_2 cells still suffer from electrolyte decomposition and insoluble Li_2O_2 clogging the pores of the air

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cathode [4,10–12]. Selecting the optimum nonaqueous solvent for rechargeable Li–air batteries is an essential prerequisite for the successful operation of Li–air batteries. Besides solvents, functional additives can be utilized to dissolve Li_2O or Li_2O_2 solid products. Lewis acid such as tris(pentafluorophenyl)borane (TPFPB) and family of boron esters are expected to dissolve LiF , Li_2O , and Li_2O_2 , which are normally insoluble in carbonate-based solvents [12–14]. Importantly, it was reported that TPFPB can partially dissolve insoluble lithium–oxygen products formed at the air cathode and thereby a more active carbon surface can be exposed for further oxygen reduction reaction (ORR) during discharge process [15,16].

Here, we report on the results of an experiment considering the influence of TPFPB-containing electrolytes on electrochemical reversibility of an electrode with Li_2O_2 as the dominant discharge product of Li–air batteries. Additionally, we analyze the effect of TPFPB on the products of Li_2O_2 -based electrodes on electrochemical reduction and oxidation.

2. Experimental

For the electrochemical tests, a composite Li_2O_2 electrode was prepared by spreading a slurry mixture of Li_2O_2 (technical grade 90 wt.%, Aldrich), poly(vinylidene fluoride) (PVDF) (KF1100, Kureha Chemical Industry), and super P (as a carbon additive for conductivity enhancement, Timcal Inc.) (35:20:45 in weight ratio) on a piece of Al foil (20 μm). The resulting electrodes were dried at 100 $^\circ\text{C}$ for 30 min. The Li_2O_2 loading was 0.13 mg cm^{-2} . The electrolyte was comprised 1.0 M LiPF_6 in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (30:70, v/v) with 5 wt.% tris(pentafluorophenyl) borane (TPFPB) (95 wt.%, Aldrich) and 3 wt.% vinylene carbonate (VC, Soulbrain Co. Ltd.). VC was used as an additive to form an effective solid electrolyte interphase (SEI) layer on the Li electrode.

Galvanostatic discharge and charge cycling (WonATech WBCS 3000 battery measurement system) was performed in the potential window from 2.0 to 4.5 V vs. Li/Li^+ using a two-electrode 2032 coin-type cell without holes for air (or O_2) permeation. Microporous polyethylene film was used as a separator. Cells were assembled in an Ar-filled glove box with less than 1 ppm of both oxygen and moisture. The Li_2O_2 electrode functioned as the working electrode and the Li metal foil as the counter electrode. In order to obtain a proper porosity, the Li_2O_2 electrode was not pressed and was spot-welded to the top of the coin cell.

After cycling, cells were carefully opened in a glove box to retrieve their electrodes, and electrodes were subsequently rinsed in dimethyl carbonate (DMC) to remove residual LiPF_6 -based electrolyte; resulting materials were dried at room temperature.

To investigate the effect of TPFPB on the dissociation of Li_2O_2 in EC/EMC solvent, ^{11}B nuclear magnetic resonance (NMR) experiments for EC/EMC/0.06 M TPFPB with and without Li_2O_2 were performed on a Bruker 500 MHz FT-NMR spectrometer. For the measurement of ex situ Raman, Attenuated Total Reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), these dried electrodes were utilized. An air-tight Raman cell, which we have developed, was assembled in a glove box filled with high purity argon gas [17]. The Raman spectra were recorded at room temperature using an NRS-5100 micro Raman spectrophotometer (Jasco International Co., Ltd.), which was equipped with a single monochromator as a laser filter. Raman spectra were excited by a 532 nm laser.

Cell impedances of 2032 coin-type cells (Li_2O_2 electrode/metallic lithium) before and after charge were monitored by means of an AC complex impedance analysis with an IVIUM frequency response analyzer over a frequency range of 50 mHz to 1 MHz.

3. Results and discussion

Fig. 1 shows a comparison of the voltage profiles of the Li_2O_2 /super P/PVDF and the super P/PVDF electrodes using different electrolytes at 23.4 mA g^{-1} during the first cycle. The large overpotential for the Li_2O_2 /super P/PVDF electrode with EC/EMC (3/7, v/v)/1 M LiPF_6 is clearly shown in Fig. 1(b) and a low charge capacity of 563 mAh g^{-1} was obtained even after charging to 4.5 V vs. Li/Li^+ . Interestingly, the addition of 5 wt.% tris(pentafluorophenyl) borane (TPFPB) to EC/EMC (3/7, v/v)/1 M LiPF_6 significantly reduced the charge potential of the Li_2O_2 electrode and led to an increased charge capacity of 1294 mAh g^{-1} , as shown in Fig. 1(a). The reduced charge potential during the first charge may be related to the improvement of the electrochemical oxidation of Li_2O_2 to Li and gaseous oxygen, which is a result of the presence of TPFPB in the electrolyte. It is supposed that the electron deficient boron center in the TPFPB interacts strongly with the O_2^{2-} in Li_2O_2 and thereby, the electrochemical oxidation of Li_2O_2 readily takes place in carbonate-based electrolytes. In order to investigate the dissociation ability of TPFPB for Li_2O_2 , the ^{11}B NMR spectra of EC/EMC/0.06 M TPFPB and EC/EMC/0.06 M Li_2O_2 with 0.06 M TPFPB were taken at room temperature, as shown in Fig. 2(a) and (b). The addition of 0.06 M TPFPB in EC/EMC with 0.06 M Li_2O_2 results in a pronounced new peak at an up field shift (–3.82 ppm), as shown in Fig. 2(b). This peak is considered to generate from the ion–dipole interaction between boron of TPFPB and O_2^{2-} of Li_2O_2 , reflecting more

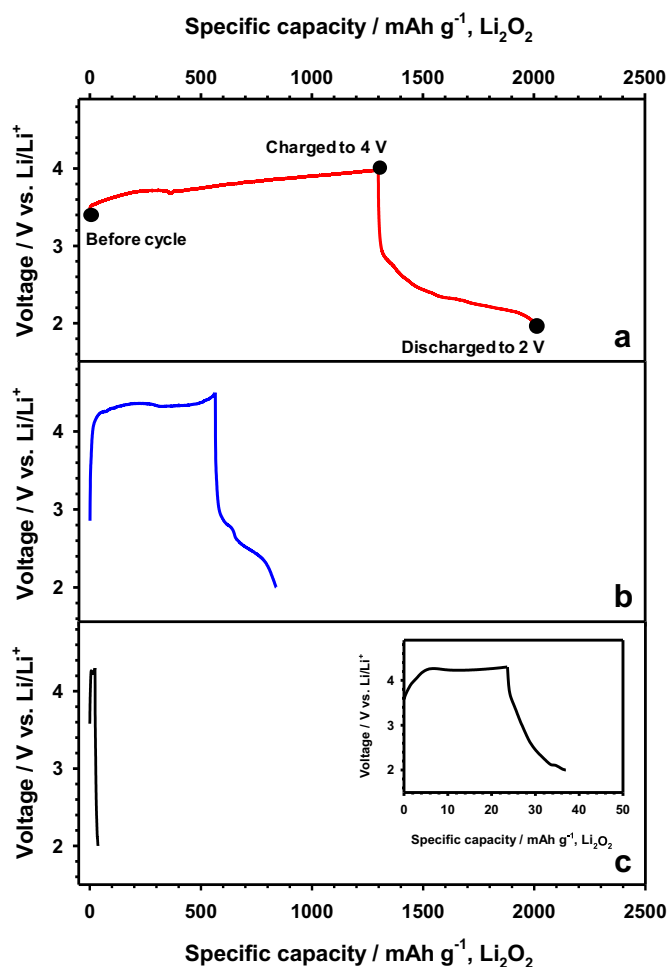


Fig. 1. The voltage profiles of (a) Li_2O_2 /Super P/PVDF electrode in EC/EMC/1 M LiPF_6 with 5 wt.% TPFPB, (b) Li_2O_2 /Super P/PVDF electrode in EC/EMC/1 M LiPF_6 , (c) Super P/PVDF electrode in EC/EMC/1 M LiPF_6 during the first cycle.

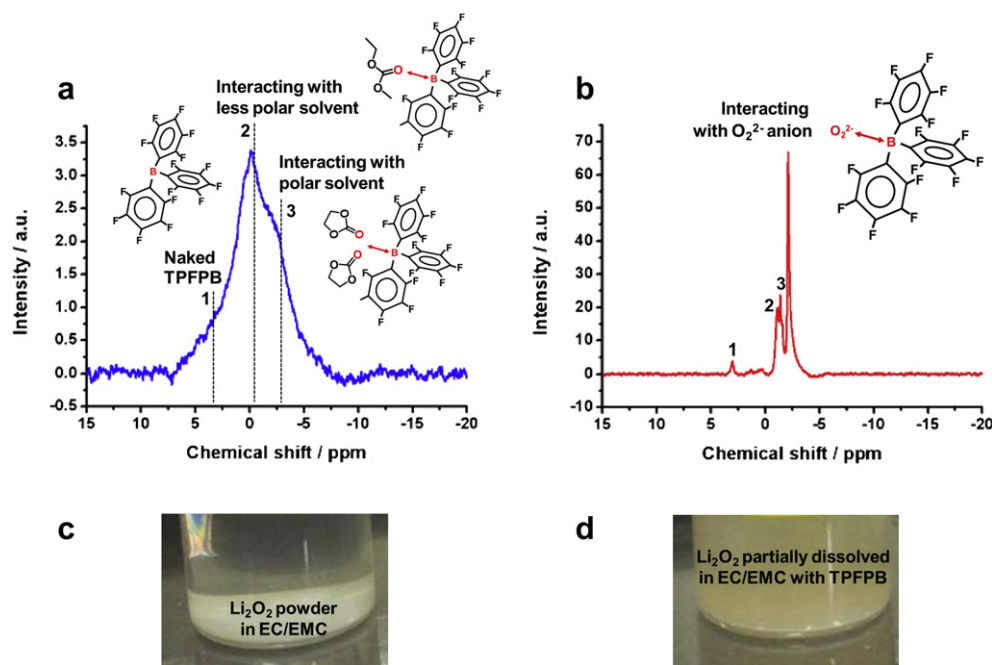


Fig. 2. ^{11}B NMR spectra of (a) 0.06 M TFPFB in EC/EMC solvent, (b) 0.06 M TFPFB/0.06 M Li_2O_2 in EC/EMC solvent. Picture of (c) 0.06 M TFPFB in EC/EMC, (d) 0.06 M TFPFB/0.06 M Li_2O_2 in EC/EMC solvent.

dominant shielding of the boron atom, as depicted in Fig. 2(b) [18]. Indeed, Li_2O_2 , which is insoluble in EC/EMC, partially dissolved in the presence of TFPFB (Fig. 2(c) and (d)). The improved dissociation of Li_2O_2 by TFPFB is thought to reduce the charge potential of Li_2O_2 cathode during the first charge. It is very important that the increase of charge potential during cycling should be suppressed in order to improve the electrochemical performances of Li–air batteries. The first discharge capacities of the Li_2O_2 /super P/PVDF electrodes with and without TFPFB are 714 mAh g^{-1} and 277 mAh g^{-1} , respectively. It should be noted that super P does not contribute to the reversible capacity, as shown in Fig. 1(c). The increased discharge capacity for Li_2O_2 /super P/PVDF electrodes with TFPFB shows that TFPFB is responsible for the electrochemical reduction of O_2 to Li_2O_2 .

To determine the composition change of the electrodes induced by Li extraction and insertion, the measurements of ex situ Raman spectroscopy and Attenuated Total Reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy were performed, as shown in Fig. 3. Fig. 3(a) presents the Raman spectra of the Li_2O_2 electrodes before cycling, after being initially charged to 4.0 V, and after discharge to 2.0 V. There is a pronounced peak centered at 789 cm^{-1} , indicating the O–O stretching of Li_2O_2 for the pristine Li_2O_2 electrode [7]. After charging to 4.0 V in the presence of TFPFB, the Raman shift of the O–O stretching in the Li_2O_2 entirely disappeared. This provides evidence that TFPFB leads to the electrochemical oxidation of Li_2O_2 to Li and gaseous oxygen during the first charge process. The peak corresponding to Li_2O_2 was observed at around 789 cm^{-1} after the cell was discharged to 2.0 V, as shown in Fig. 3(a). From this result,

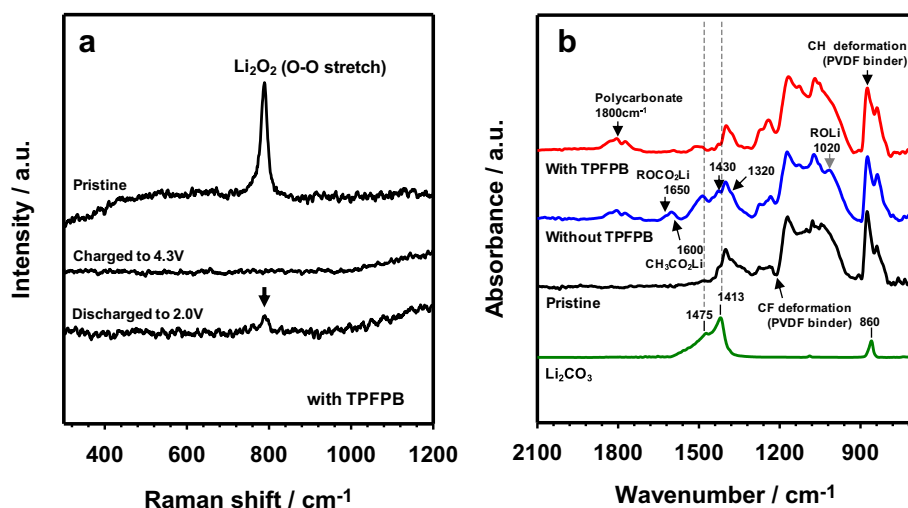


Fig. 3. Characteristics of Li_2O_2 -based electrodes before and after cycle. (a) Raman spectra of Li_2O_2 /Super P/PVDF electrode, (b) ATR–FTIR spectra of Li_2O_2 /Super P/PVDF electrode before cycle (black line), after charged in TFPFB free electrolyte (blue line), and after charged in TFPFB-containing electrolyte (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

it is clear that TFPFB allows the formation of Li_2O_2 via electrochemical reaction of Li with gaseous oxygen. Because the composition of the surface films plays a significant role in determining the electrochemical performance of the electrodes, it is necessary to understand the surface chemistry of the Li_2O_2 -based electrodes in the electrolytes. Fig. 3(b) shows ATR–FTIR spectra of the Li_2O_2 -based electrodes charged in electrolytes with and without TFPFB. The main spectral features measured from the Li_2O_2 -based electrode charged in TFPFB-free electrolyte indicate the peaks of ROCO_2Li ($1650, 1430\text{ cm}^{-1}$), Li_2CO_3 ($1475, 1413\text{ cm}^{-1}$), and ROLi (1020 cm^{-1}) surface species, including polycarbonates (around 1800 cm^{-1}) produced by the VC reduction, as depicted in Fig. 3(b) [19]. It was reported that the characteristic feature of the VC polymer (polycarbonate) is observed at the surface of the cathode with the VC-containing electrolyte [20]. As clearly seen in Fig. 3(b), the introduction of TFPFB favorably mitigated the formation of ROCO_2Li , Li_2CO_3 , and ROLi during the first charge process. This means that TFPFB effectively reduces the charge potential for electrochemical oxidation of Li_2O_2 and thereby hinders the electrochemical decomposition of EC and EMC on the Li_2O_2 -based electrode.

The XPS spectra of the Li_2O_2 -based electrodes charged in electrolytes with and without TFPFB are shown in Fig. 4. The Li 1s spectra of the Li_2O_2 cathodes display a convolution of two peaks as well as the fitting curves for the TFPFB-free electrolyte. The peaks centered

at 55.4 eV and 54.7 eV are assigned to Li_2CO_3 and Li_2O_2 , respectively, as shown in the Li 1s spectra (Fig. 4(b)). The main reason for the presence of a peak corresponding to Li_2O_2 on the Li_2O_2 -based electrode charged in TFPFB-free electrolyte is the difficulty of the electrochemical oxidation of Li_2O_2 during the first charge. The Li_2CO_3 surface species mostly originate from the decomposition of ethylene carbonate (EC) when charged to 4.5 V vs. Li/Li^+ . For the Li_2O_2 -based electrode with TFPFB, the peak corresponding to LiF (56 eV) is predominantly shown in Fig. 4(b). This means that the SEI formed on the Li_2O_2 -based electrode mainly consists of LiF and TFPFB mitigates the formation of Li_2CO_3 by the electrochemical decomposition of EC and EMC. The F 1s spectrum in Fig. 4(c) exhibits the peak centered at around 685.6 eV, which is attributable to LiF. From the XPS results, it is thought that the surface layer of the Li_2O_2 -based electrode charged in the TFPFB-containing electrolyte is mostly composed of LiF formed by the electrochemical decomposition of TFPFB, as depicted in Fig. 5. The P 2p spectra of the Li_2O_2 -based electrodes without TFPFB reflect the obvious formation of surface species related to the decomposition of the PF_6^- anion. Possible anion decomposition products include Li_xPF_y and Li_xPOF_y species [21]. Comparing the P 2p spectra reveals that TFPFB decreases the formation of Li_xPF_y and Li_xPOF_y species by the decomposition of the PF_6^- anion. This is likely because the electron deficient boron center in TFPFB interacts with the PF_6^- anion and impedes the electrochemical decomposition of the anion. The B 1s

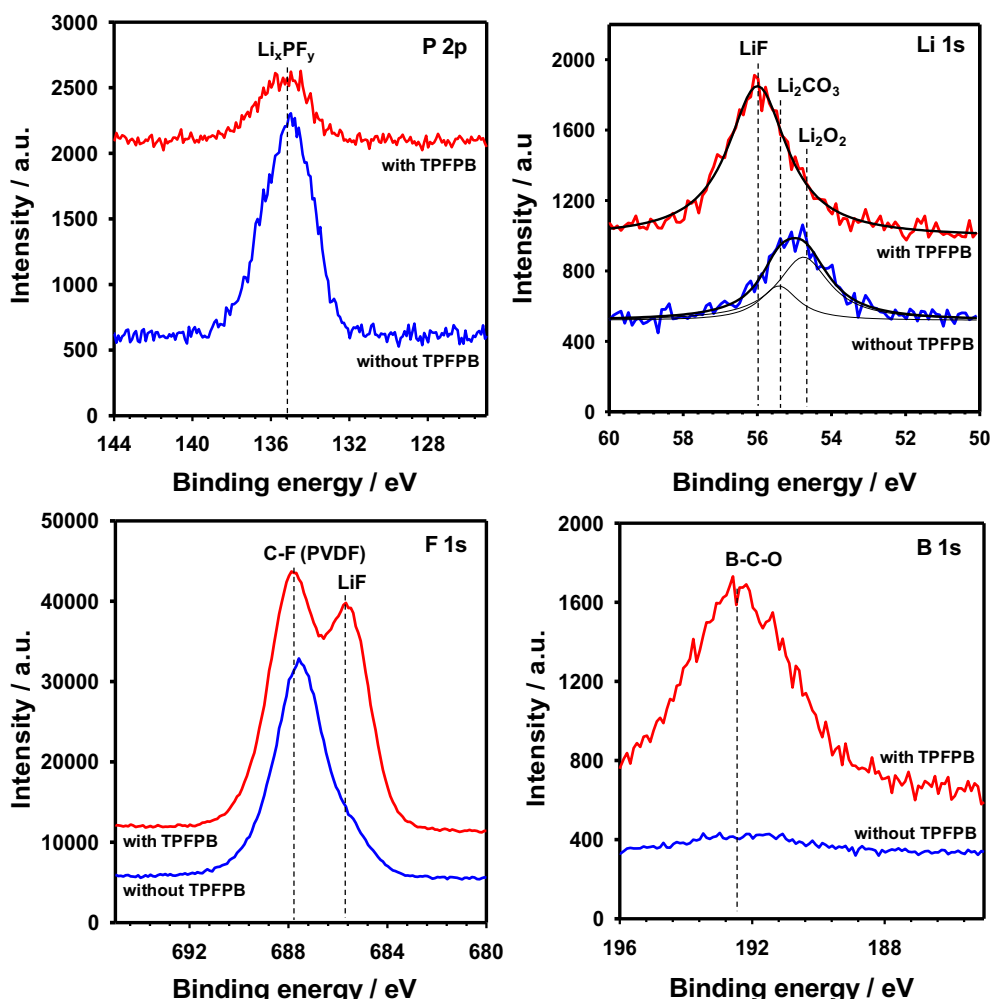


Fig. 4. P 2p, Li 1s, F 1s, and B 1s XPS spectra for the surface of Li_2O_2 /Super P/PVDF electrode after charging. Black lines represent curve fitting results.

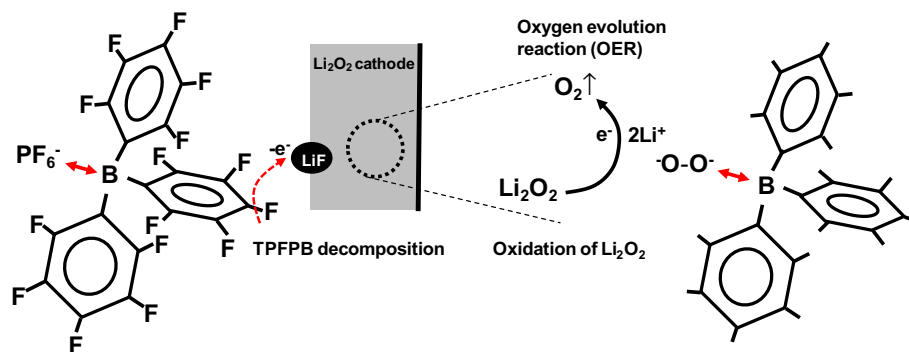


Fig. 5. Schematic drawing for the role of TPFPB on the oxidation of Li_2O_2 to O_2 during charge.

XPS spectra of Fig. 4 show the peak attributed to boron-based compounds at 192.5 eV. This implies that TPFPB undergoes electrochemical decomposition at the Li_2O_2 –electrolyte interface during cycling. Electrochemically stable Lewis acid with electron deficient atom is thought to be one of the promising materials for high performance Li– O_2 batteries.

Fig. 6(a) shows the charge–discharge curves of Li_2O_2 -based electrode/Li coin-type cells with and without TPFPB. Because the cells have no holes for air permeation, O_2 evolved from the electrochemical oxidation of the Li_2O_2 -based electrode within the cell is utilized for cycling. Even though the charge and discharge capacities were gradually decreased, it is clear that the presence of TPFPB leads to a reversible electrochemical oxidation and reduction of Li_2O_2 during cycling. Fig. 6(b) and (c) presents the contribution to the cell impedance from three components: the

intercept at high frequency for the ohmic resistance of a cell, the impedance associated with Li^+ migration across the SEI, and the resistance for the faradaic charge transfer reaction at low frequency. The electrochemical impedance spectra reveal that total resistance of a cell with TPFPB ($141\ \Omega$) was much lower than that of a cell without TPFPB ($174\ \Omega$) before charge. This difference is likely because TPFPB can interact with Li_2O_2 and reduce the charge transfer reaction resistance. In addition, we carried out the EIS measurements for cells with and without TPFPB after charged up to similar charge capacity of $560\ \text{mAh g}^{-1}$. The interfacial resistance (surface film resistance and charge transfer reaction resistance) of a cell without TPFPB largely increased compared to a cell with TPFPB, as displayed in Fig. 6(b) and (c). It is clear that TPFPB is responsible for reducing the interfacial resistance and the charge potential of cells. It is found that the discharge potential

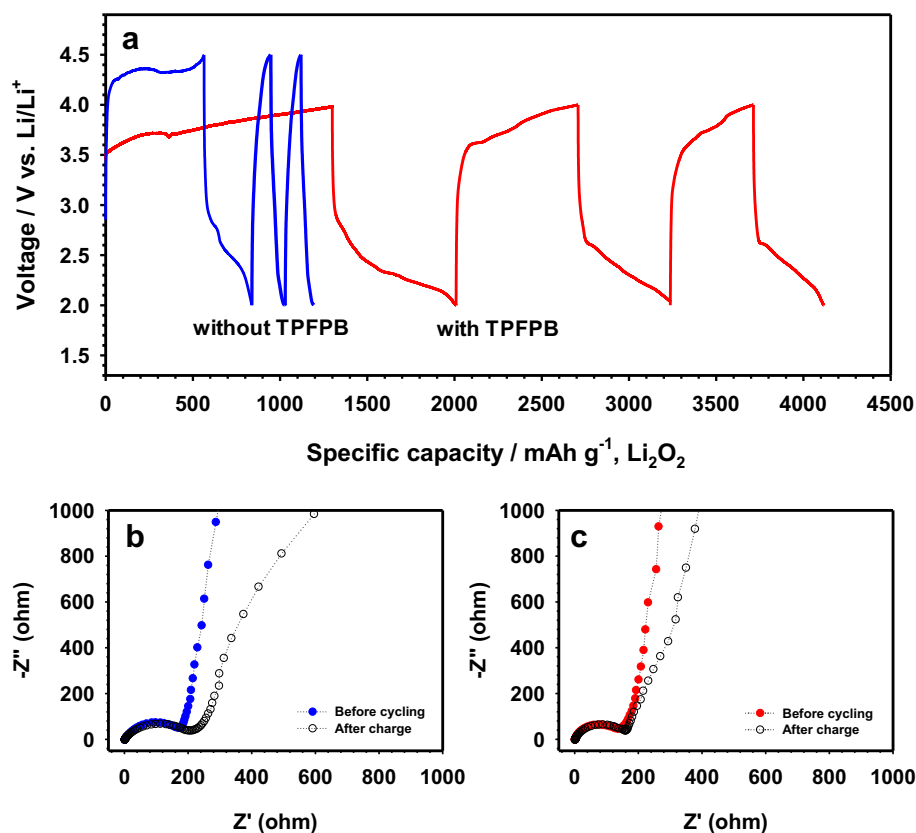


Fig. 6. (a) Charge and discharge profiles of the Li_2O_2 /Super P/PVDF electrode with and without TPFPB for a current density of $23.4\ \text{mA g}^{-1}$, electrochemical impedance spectra of Li_2O_2 cells (b) without TPFPB, (c) with TPFPB before and after charge.

plateau for the oxygen reduction reaction (ORR) is analogous for cells with and without TPFPB. A plausible explanation for this behavior would be the TPFPB decomposition at the Li_2O_2 electrode. The decomposition product of TPFPB may increase cell impedance and some part of TPFPB cannot act as a Lewis acid helping the dissociation of Li_2O_2 . Therefore, it is thought that TPFPB is more effective for the oxygen evolution reaction (OER) because of the reduced charge potential and the similar discharge potential compared to TPFPB-free cells.

4. Conclusion

We found that TPFPB drastically reduced the charge potential for the electrochemical oxidation of Li_2O_2 . The ex situ Raman results could confirm that the electrochemical oxidation of Li_2O_2 to Li and O_2 effectively occurs in TPFPB-containing electrolytes during the first charging process and a Raman peak assigned to Li_2O_2 was recovered after discharge to 2.0 V. Also, using ex situ ATR–FTIR and XPS, we found that TPFPB-containing electrolytes mitigate the formation of ROCO_2Li , Li_2CO_3 , and ROLi by the electrochemical decomposition of carbonate solvents.

Acknowledgments

This research was supported by the MKE (The Ministry of Knowledge Economy), Korea, under the ITRC (Information Technology Research Center) support program supervised by the NIPA (National IT Industry Promotion Agency) (NIPA-2012-H0301-12-1009) and the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2011-C1AAA001-0030538).

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